Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information (ESI)

Mixed-ligand coordination polymers from 1,2-bis(1,2,4-triazol-4-yl)ethane and benzene-1,3,5-tricarboxylate: Trinuclear nickel or zinc secondary building units for three-dimensional networks with crystal-to-crystal transformation upon dehydration

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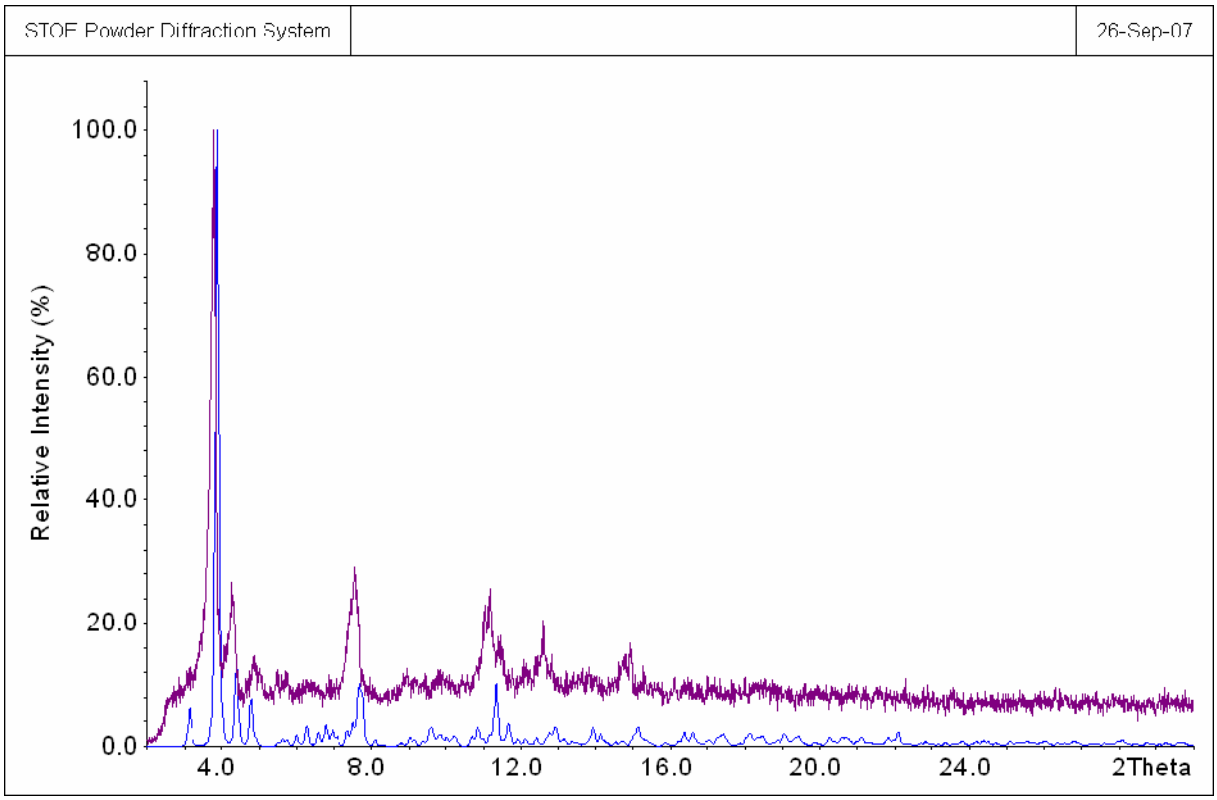


Fig. S1 X-ray powder diffractogram. Blue curve is simulated from single-crystal X-ray data of $^{3}_{\infty}\{[Ni_3(\mu_3\text{-btc})_2(\mu_4\text{-btre})_2(\mu\text{-}H_2O)_2]\cdot\sim 20H_2O\}$, **1**. Purple curve is measured on a crystal sample of **1** which was separated from mother liquor by filtration within one minute without extensive drying ("moist sample") and with no grinding.

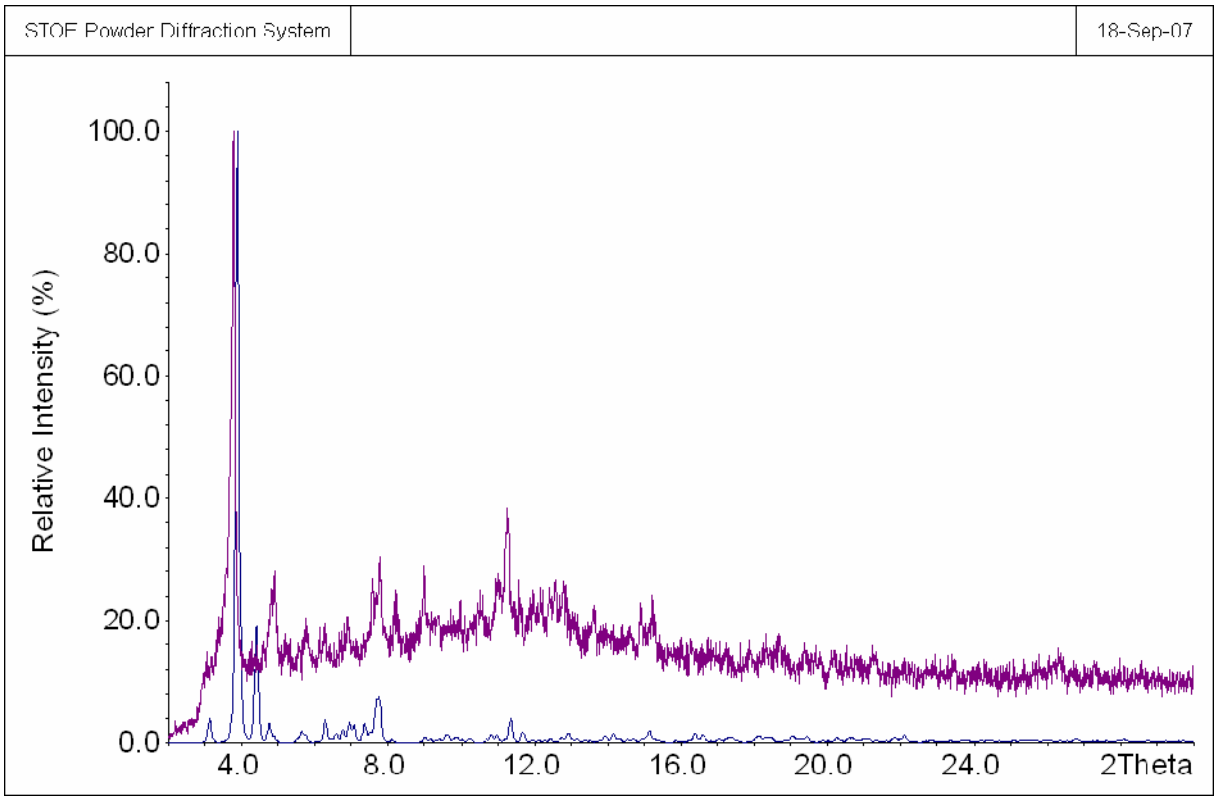


Fig. S2 X-ray powder diffractogram. Blue curve is simulated from solvent-depleted single-crystal X-ray data of $^{3}_{\infty}\{[Ni_3(\mu_3\text{-btc})_2(\mu_4\text{-btre})_2(\mu\text{-}H_2O)_2]\}$, **1** – $20H_2O$. Purple curve is measured on a dried sample of **1** with almost no grinding.

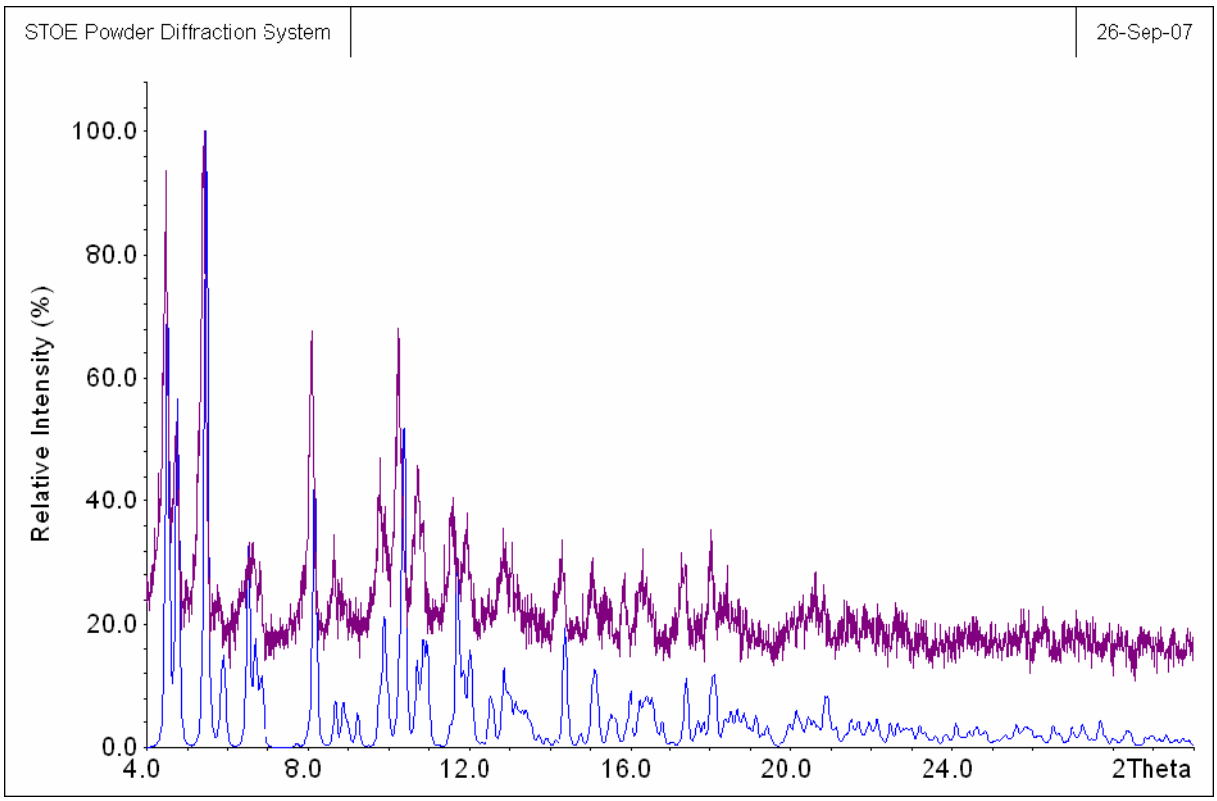


Fig. S3 X-ray powder diffractogram. Blue curve is simulated from single-crystal X-ray data of $^{3}_{\infty}\{[Ni_3(\mu_2\text{-btc})_2(\mu_4\text{-btre})_2(\mu\text{-}H_2O)_2(H_2O)_2]\cdot 4H_2O\}$, **2**. Purple curve is measured on a crystal sample of **2**.

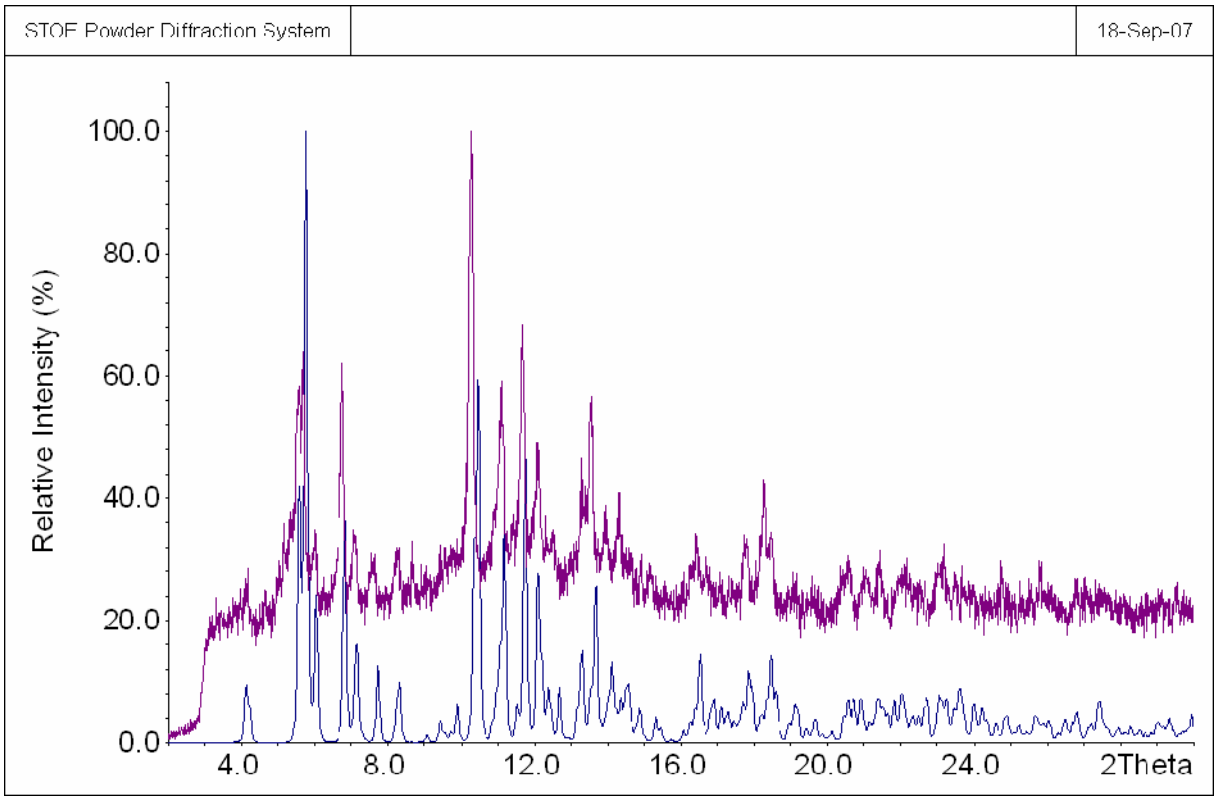


Fig. S4 X-ray powder diffractogram. Blue curve is simulated from single-crystal X-ray data of $^{3}_{\infty}\{[Zn_3(\mu_4\text{-btc})_2(\mu_4\text{-btre})(H_2O)_2] \cdot 2H_2O\}$, **3**. Purple curve is measured on an air-dried sample of **3**.

The following pages contain the experimental nitrogen adsorption isotherm of an evacuated, dried sample of compound **1** (after 3 days at 50 °C):

- isotherm with volume versus relative pressure (p/p_0)
- iotherm with volume versus log (p/p_0)
- adsorption pore volume versus diameter (in Å)
- adsorption surface area versus diameter (in Å)

as Figures S5 to S8

Date: 02/27/07 Page 1

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Micropore Version 2.40

Sample ID..... 146 Vakuum
Sample Description..... nach 50C 3 tage
Comments.....
Gas Type..... Nitrogen

Cross-Sec Area..	16.2	Å²	Corr Factor..	6.580E-05		Molec Wgt..	28.0134
Sample Weight...	0.0180	g	P/Po Toler...	3		File Name..	146VAC.RAW
Analysis Time...	281.2	min	Equil Time...	2		Operator...	
Outgas Time.....	0.0	hrs	Outgas Temp..	0	°C	Station #..	1

End of Run..... 02-27-07 07:38am

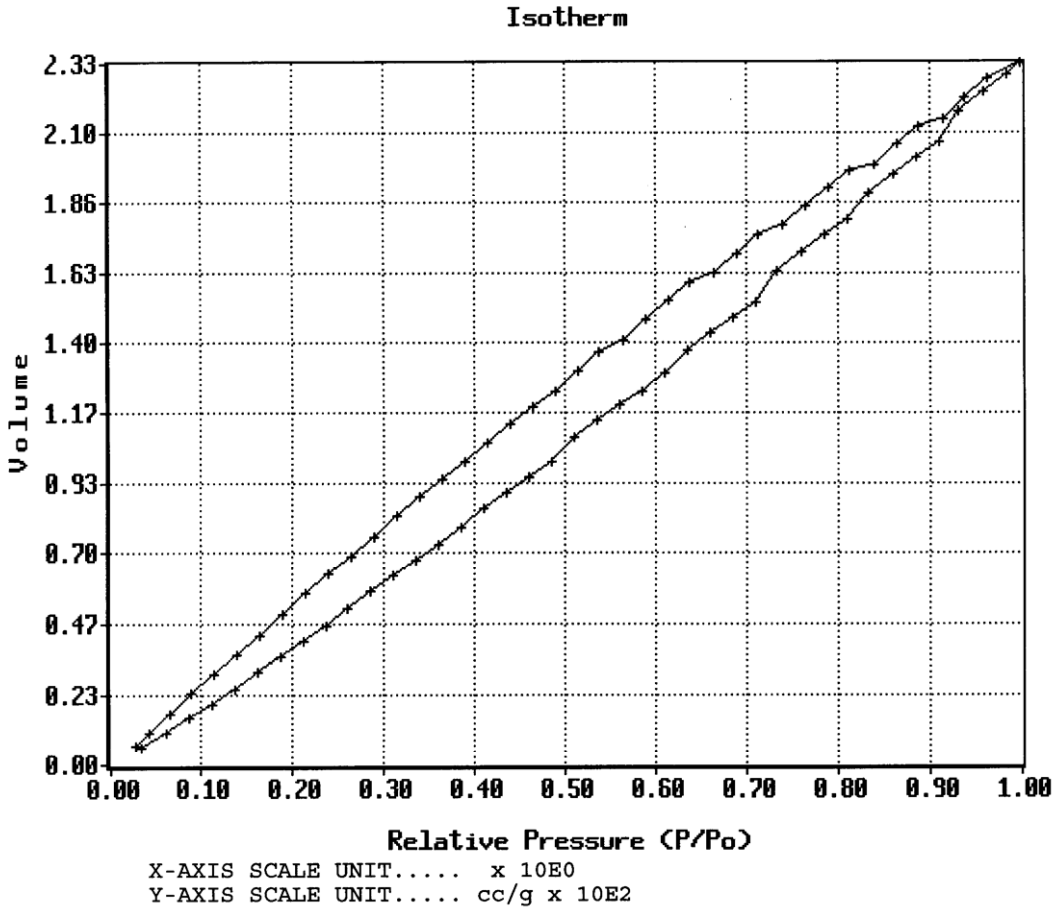


Fig. S5 Experimental nitrogen adsorption isotherm with volume versus relative pressure (p/p_0) of an evacuated, dried sample of compound **1** (after 3 days at 50 °C).

Date: 02/27/07 Page 1

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Micropore Version 2.40

Sample ID.....	146 Vakuum						
Sample Description.....	nach 50C 3 tage						
Comments.....							
Gas Type.....	Nitrogen						
Cross-Sec Area..	16.2	Å²	Corr Factor..	6.580E-05		Molec Wgt..	28.0134
Sample Weight...	0.0180	g	P/Po Toler...	3		File Name..	146VAC.RAW
Analysis Time...	281.2	min	Equil Time...	2		Operator...	
Outgas Time.....	0.0	hrs	Outgas Temp..	0	°C	Station #..	1
End of Run.....	02-27-07 07:38am						

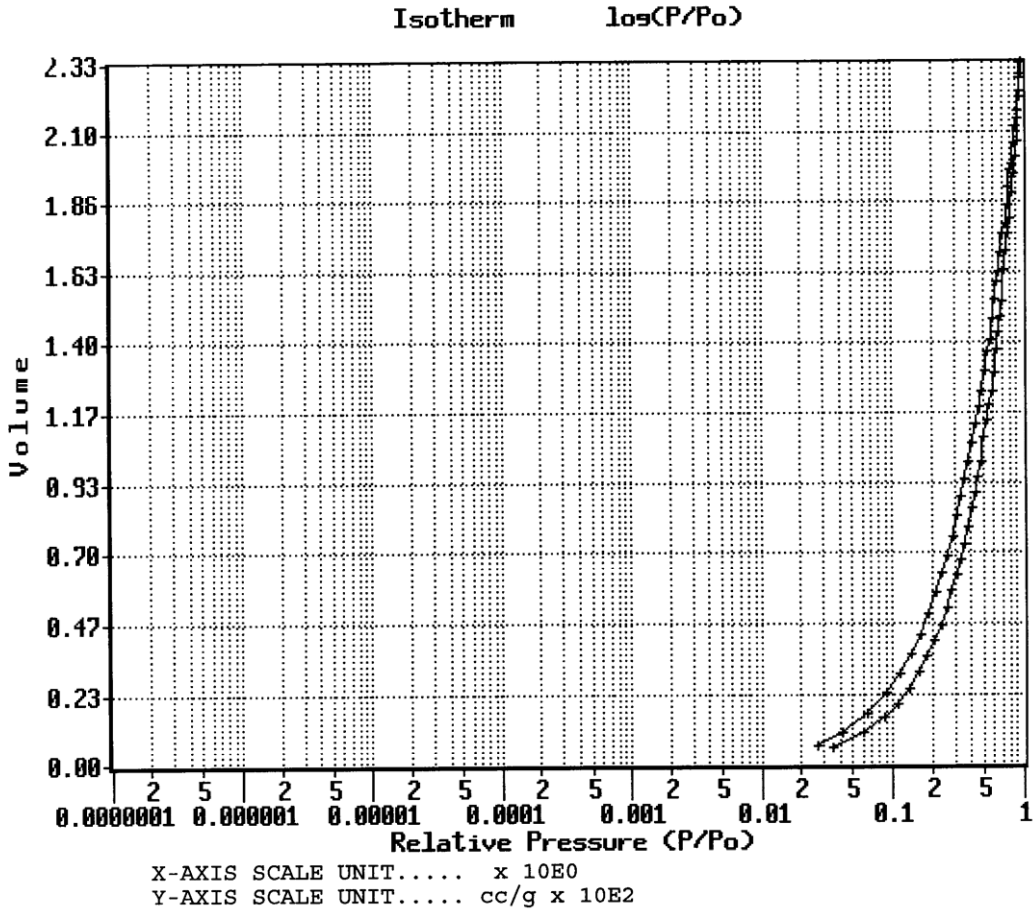
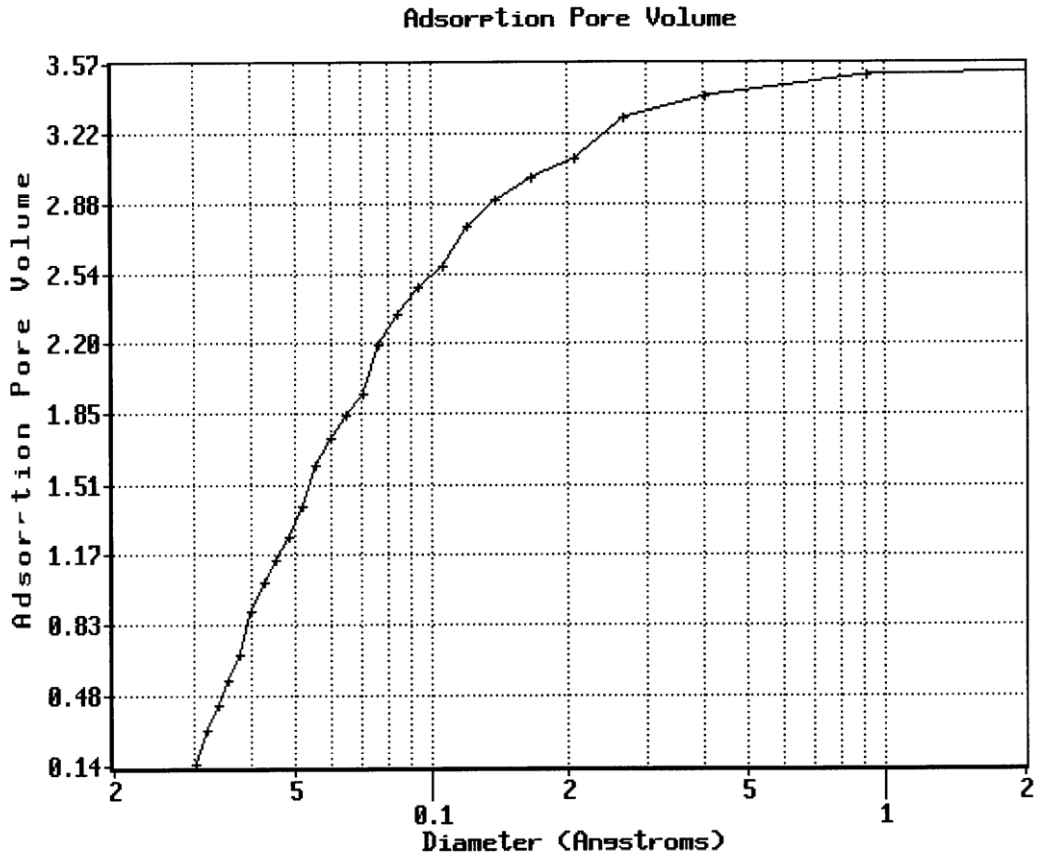


Fig. S6 Experimental nitrogen adsorption isotherm with volume versus log (p/p_0) of an evacuated, dried sample of compound **1** (after 3 days at 50 °C).

Date: 02/27/07 Page 2

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Micropore Version 2.40

Sample ID.....	146 Vakuum						
Sample Description.....	nach 50C 3 tage						
Comments.....							
Gas Type.....	Nitrogen						
Cross-Sec Area..	16.2	Å²	Corr Factor..	6.580E-05		Molec Wgt..	28.0134
Sample Weight...	0.0180	g	P/Po Toler...	3		File Name..	146VAC.RAW
Analysis Time...	281.2	min	Equil Time...	2		Operator...	
Outgas Time.....	0.0	hrs	Outgas Temp..	0	°C	Station #..	1
End of Run.....	02-27-07 07:38am						



X-AXIS SCALE UNIT..... Angstroms x 10E3
Y-AXIS SCALE UNIT..... cc/g x 10E-1

Fig. S7 Experimental nitrogen adsorption adsorption pore volume versus diameter (in Å) of an evacuated, dried sample of compound **1** (after 3 days at 50 °C).

Date: 02/27/07 Page 2

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Micropore Version 2.40

Sample ID.....	146 Vakuum						
Sample Description.....	nach 50C 3 tage						
Comments.....							
Gas Type.....	Nitrogen						
Cross-Sec Area..	16.2	Å²	Corr Factor..	6.580E-05		Molec Wgt..	28.0134
Sample Weight...	0.0180	g	P/Po Toler...	3		File Name..	146VAC.RAW
Analysis Time...	281.2	min	Equil Time...	2		Operator...	
Outgas Time.....	0.0	hrs	Outgas Temp..	0	°C	Station #..	1
End of Run.....	02-27-07 07:38am						

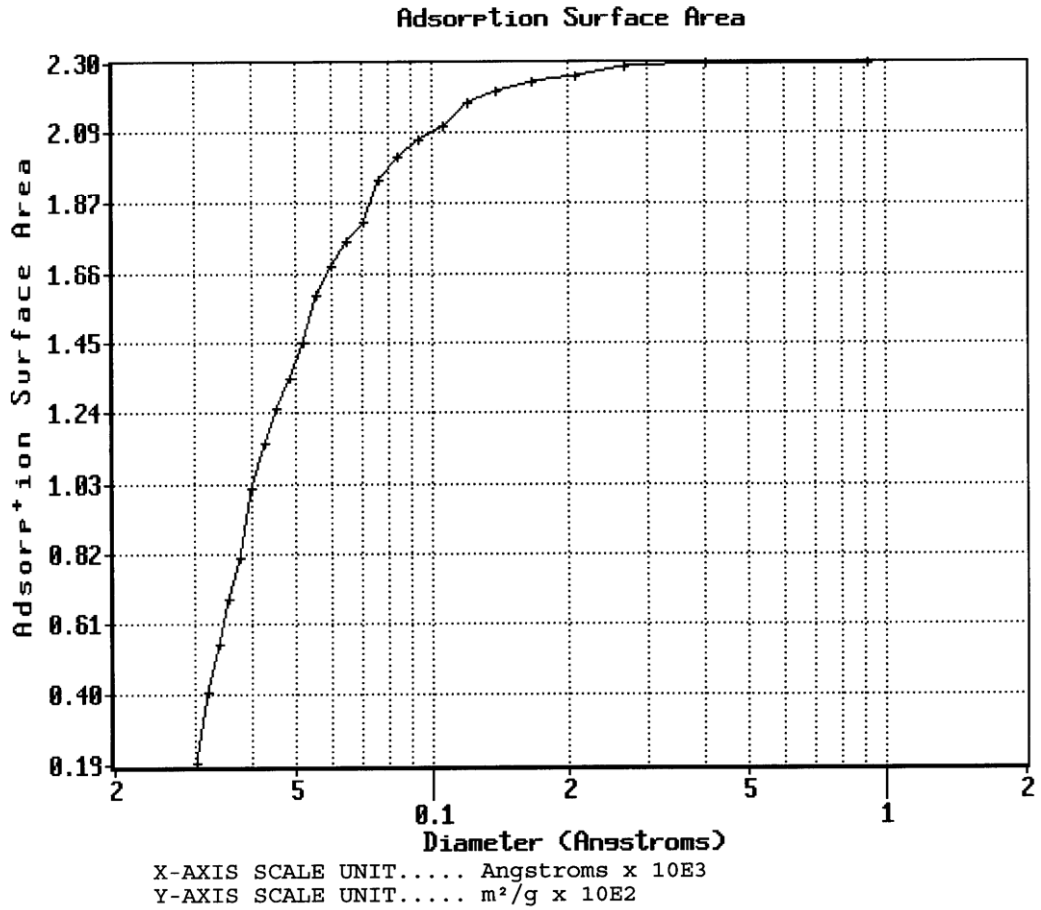


Fig. S8 Experimental nitrogen adsorption isotherm adsorption surface area versus diameter (in Å) of an evacuated, dried sample of compound **1** (after 3 days at 50 °C).

Table S1 Hydrogen bonding interactions in $^{3}_{\infty}\{[Ni_3(\mu_3\text{-btc})_2(\mu_4\text{-btre})_2(\mu\text{-}H_2O)_2]\cdot\sim 20H_2O\}$, **1**.[a)]

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
from aqua ligand				
O1–H1A···O3	0.94(3)	1.61(3)	2.531(2)	166(3)
O1–H1B···O7^{2}	0.86(3)	1.69(4)	2.536(3)	168(3)

[a)] D = Donor, A = acceptor. For found and refined atoms the standard deviations are given. Symmetry relations: 2 = x, –0.5–y, 0.5+z.

Table S2 Hydrogen bonding interactions in $^{3}_{\infty}\{[Ni_3(\mu_2\text{-btc})_2(\mu_4\text{-btre})_2(\mu\text{-}H_2O)_2]\cdot 4H_2O\}$, **2**.[a)]

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
from aqua ligands				
O1–H1A···O6^{2}	0.86(5)	2.22(8)	2.965(11)	144(10)
O1–H1A···O7$^{3'}$	0.86(5)	2.41(11)	2.833(11)	111(9)
O1–H1B···O3	0.84(5)	1.70(6)	2.516(9)	163(12)
O1–H1B···O2	0.84(5)	2.67(11)	3.052(10)	109(9)
O8–H8A···O6^{2}	0.98(5)	1.57(6)	2.532(13)	165(13)
O8–H8B···O5$^{1'}$	0.80(14)	2.15(14)	2.789(13)	137(14)
O8–H8B···O4$^{1'}$	0.80(14)	2.77(15)	2.822(13)	85(11)
from crystal water				
O9–H9A···O10	0.93	2.09	2.830(16)	135.6
O9–H9B···O2$^{3''}$	0.94	2.31	2.896(12)	120.1
O9–H9B···O4$^{2''}$	0.94	2.46	3.365(12)	160.5
O10–H10A···O9$^{1''}$	0.90	1.98	2.754(16)	143.2
O10–H10B···O5$^{1'}$	0.95	2.13	3.043(16)	161.1

[a)] D = Donor, A = acceptor. For found and refined atoms the standard deviations are given. Symmetry relations: 1' = 1–x, 1–y, 1–z; 1'' = 1–x, 1–y, 2–z; 2 = x, 0.5–y, z+0.5; 2'' = +x, 1.5–y, 0.5+z; 3' = –x, –0.5+y, 0.5–z; 3'' = 1–x, 0.5+y, 1.5–z;

Table S3 Selected Bonds Angles (°) in **1** and **2.**[a]

	1	**2**
O1–Ni1–O2	91.2(1)	91.3(2)
O1–Ni1–O4$^{1'}$	177.0(1)	176.2(3)
O1–Ni1–O6^{2} / O8 [b]	92.3(1)	93.9(3)
O2–Ni1–O4$^{1'}$	86.2(1)	87.3(3)
O2–Ni1–O6^{2} / O8 [b]	90.9(1)	87.1(3)
O4$^{1'}$–Ni1–O6^{2} / O8 [b]	89.2(1)	89.6(3)
N1–Ni1–O1	84.0(1)	84.2(3)
N1–Ni1–O2	87.5(1)	85.4(3)
N1–Ni1–O4$^{1'}$	94.4(1)	92.1(3)
N1–Ni1–O6^{2} / O8 [b]	176.0(1)	172.2(3)
N6–Ni1–O1	83.5(1)	83.8(3)
N6–Ni1–O2	174.7(1)	171.8(3)
N6–Ni1–O4$^{1'}$	99.1(1)	97.2(3)
N6–Ni1–O6^{2} / O8 [b]	89.2(1)	99.7(3)
N1–Ni1–N6	92.0(1)	87.6(3)
O1–Ni2–N2	85.4(1)	84.2(3)
O1–Ni2–N2^{1}	94.7(1)	95.8(3)
O1–Ni2–N5	85.2(1)	84.0(3)
O1–Ni2–N5^{1}	94.8(1)	96.1(3)
N2–Ni2–N5	90.5(1)	89.5(3)
N2–Ni2–N5^{1}	89.5(1)	90.5(3)
Ni2–O1–Ni1	107.7(1)	107.6(3)

[a] Symmetry relations in **1**: 1 = –x, –y, –z; 1' = 1–x, –y, –z; 2 = x, –0.5–y, 0.5+z; in **2**: 1 = –x, 1–y, 1–z; 1' = 1–x, 1–y, 1–z. [b] O6^{2} in **1** and O8 in **2**.

Table S4 Hydrogen bonding interactions in $^{3}_{\infty}\{[Zn_3(\mu_4\text{-btc})_2(\mu_4\text{-btre})(H_2O)_2] \cdot 2H_2O\}$, **3**. [a)]

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
from aqua ligands				
O1–H1A···O23^{1}	0.80(3)	1.89(3)	2.678(2)	168(3)
O1–H1B···O24^{2}	0.95(3)	1.74(3)	2.677(2)	171(2)
O2–H2A···O16$^{1'}$	0.80(3)	2.02(3)	2.813(2)	168(3)
O2–H2B···O16$^{2'}$	0.93(3)	1.75(3)	2.668(2)	170(3)
from crystal water				
O3–H3C···O22	0.84(4)	2.04(4)	2.865(3)	164(4)
O3–H3D···O2$^{1''}$	0.83(4)	2.38(4)	3.096(3)	144(4)
O4–H4A···O1$^{1'''}$	0.81(3)	2.58(4)	3.141(3)	128(4)
O4–H4B···O14	0.79(4)	2.05(4)	2.820(3)	165(4)

[a)] D = Donor, A = acceptor. For found and refined atoms the standard deviations are given. Symmetry relations:
1 = 1+x, y, z; 1' = –1+x, y, z; 1'' = x, 1+y, 1+z; 1''' = x, –1+y, –1+z;
2 = –x, 2–y, 1–z; 2' = 1–x, 2–y, –z;

Table S5 Crystal data and structure refinement for thermally treated crystals of **3**.

Compound	**3** – no thermal treatment	**3** – dried at 35 °C and 1.5 mbar for 6 h prior to the X-ray data collection.	**3** – dried at 100 °C and $1 \cdot 10^{-4}$ mbar (diffusion pump) for 6 h prior to the X-ray data collection.	**3** – dried at 35 °C and 1.5 mbar for 6 h prior to the X-ray data collection. **halved unit cell** [e]
Empirical formula	$C_{24}H_{22}N_6O_{16}Zn_3$	$C_{24}H_{22}N_6O_{16}Zn_3$	$C_{24}H_{22}N_6O_{16}Zn_3$	$C_{24}H_{22}N_6O_{16}Zn_3$
M/g mol^{-1}	846.59	846.59	846.59	846.59
Crystal size/mm	0.40 x 0.40 x 0.30	0.42 x 0.18 x 0.04	0.25 x 0.17 x 0.04	0.42 x 0.18 x 0.04
θ range/°	3.8 – 53.2	3.86 – 54.8	3.86 – 54.8	4.1 – 54.8
h; k; l range	±14; ±15; ±15	±15; ±15; ±16	±15; ±15; ±16	±15; ±15; ±16
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P–1	P–1	P–1	P–1
a/Å	11.8109(2)	11.7994(4)	11.8033(8)	7.3034(2)
b/Å	11.9995(2)	11.9776(4)	11.9829(9)	9.6603(3)
c/Å	12.4175(3)	12.4136(4)	12.4230(15)	9.8852(5)
α/°	109.0470(10)	109.048(2)	108.993(6)	87.158(2)
β/°	105.8250(10)	105.841(2)	105.919(5)	86.985(4)
γ/°	110.9600(10)	110.9620(2)	110.977(4)	86.979(3)
V/Å^3	1394.08(5)	1389.47(8)	1391.1(2)	694.73(5)
Z	2	2	2	1
T/K	203(2)	203(2)	203(2)	203(2)
D_{calc}/g cm^{-3}	2.017	2.023	2.021	2.024
F (000)	852	852	852	426
μ/mm^{-1}	2.655	2.664	2.661	2.664
Max/min transmiss.	0.451/0.360	0.901/0.401	0.901/0.5559	0.901/0.401
Refl. collected (R_{int})	26451 (0.0371)	28707 (0.0442)	29309 (0.0418)	14325 (0.0380)
Indep. reflections	5757	6318	6334	3169
Obs. refl.. [$I > 2\sigma(I)$]	4726	5312	5134	2885
Parameters refined	466	466	466	235
Max./min. $\Delta\rho$ /e Å^{-3} [a]	0.466/–0.633	0.609/–0.475	0.374/–0.344	0.893/–0.744
R_1/wR_2 [$I > 2\sigma(I)$] [b]	0.0274/0.0733	0.0272/0.0687	0.0273/0.0649	0.0363/0.0887
R_1/wR_2 (all reflect.) [b]	0.0382/0.0793	0.0356/0.0727	0.0388/0.0709	0.0404/0.0914
Goodness-of-fit on F^2 [c]	1.040	1.014	1.021	1.045
Weight. scheme w; a/b [d]	0.0440/0.0306	0.0355/0.3566	0.0321/0.6420	0.0319/1.9953

[a] Largest difference peak and hole. – [b] $R_1 = [\Sigma(\| F_o \| - \| F_c \|)/\Sigma \| F_0 \|]$; $wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$. – [c] Goodness-of-fit = $[\Sigma [w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$. – [d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2)/3$.

[e] Note: After the thermal treatment structure refinement was also possible in a halved unit cell. This resulted, however, in larger and more anisotropic temperature factors of various atoms and somewhat higher R-values. Several atoms have large maximum and minimum main axis ADP ratios (Angstrom Units) which may indicate unresolved disorder and result in prolate appearance of the ellipsoid. Large Ueq(max)/Ueq(min) ratios are found for different atoms types.